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CORROSION BEHAVIOR OF CERIUM-BASED CONVERSION COATINGS ON MAGNESIUM ALLOYS EXPOSED TO AMBIENT CONDITIONS

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Abstract

Exposure of CeCCs on AZ31B and AZ91D Mg alloys to ambient sunlight, temperature, and humidity was done to determine the effect on corrosion resistance. It was found that the CeCCs changed from pale yellow to almost translucent after 24 hours of sunlight exposure. The effect of the solar electromagnetic radiation on the morphological, chemical and optical properties of these coatings was investigated using SEM and UV-Vis characterization techniques. In addition, the corrosion performance of CeCCs before and after ambient exposure was studied by ASTM B117 neutral spray testing and electrochemical polarization measurements. In general, the changes in appearance did not adversely affect the corrosion performance of the coatings.

Introduction

The development of environmentally benign coating systems is one of the most active areas of research in surface engineering. Chromium and fluorine-free surface treatments have been the main objectives in the research and development of new coating alternatives [1-5]. A global effort has led to the development of a large number of more environmentally friendly conversion coatings such as stannates, phosphates, zirconium and rare earth-based coatings [1,2,4-6]. In addition to replacement of the hexavalent chromium and fluorine baths, the use of lightweight materials is desirable for a number of reasons. For instance, magnesium alloys have been selected by the automotive industry for several lightweight applications [3]. Cerium-based conversion coatings have shown to improve the corrosion resistance of several magnesium alloys [6-9]. The effectiveness of the CeCCs on the corrosion protection has been highly dependent on process parameters. Detailed studies of the effect of process variables such as coating thickness, CeCC bath temperature, alkaline and acid surface pretreatments, and postreatments on the corrosion performance of CeCCs applied on AZ31B and AZ91D Mg alloys have been reported [8-12]. However, effects of several concomitant variables on the behavior of CeCCs are still unknown. In this study, the effect ambient sunlight of cerium-based conversion coatings applied to AZ31B and AZ91D Mg alloys was investigated.

Experimental Procedure

Coupons of AZ31B and AZ91D Mg alloys of 10 x 5 cm^2 of exposed surface area were mechanically polished using 180 grit abrasive silicon carbide papers, cleaned with isopropyl alcohol, then rinsed with deionized water, and finally dried at room temperature. The cleaned samples were pretreated in 1 wt% HNO_3 aqueous solution for 30 seconds followed by an alkaline cleaning in 5 wt% of $Na_2SiO_3 \cdot 5H_2O$ aqueous solution for 5 minutes at room temperature. The activated Mg alloys were then immersed in an aqueous solution of 4wt% of $CeCl_3 \cdot 7H_2O$ (99.9 %, Alfa Aesar), 6 vol% of hydrogen peroxide (Fisher Chemical, 30 vol%), and 0.25 wt% of organic gelatin (RDH, Rousselot) in deionized (DI) water for 60 seconds. Following deposition, the coated samples were postreated for 5 min at 85 °C in a 2.5 wt% NaH_2PO_4 aqueous solution.

Four samples for each Mg alloy were deposited in order to have reproducible results. Two of the samples for each alloy were used for salt spray testing and the other two for the other characterization techniques. Half of the total area in each sample was wrapped with aluminum foil to protect that region from sunlight exposure. The panels were then exposed to ambient conditions during 6 hours/day (9:00 am to 3:00 pm) for consecutive 4 days.

Morphological characterization was performed using the Dual Beam Helios NanoLab 600 in SEM mode. Ultraviolet-visible spectra analyses were measured using a Varian Cary 5 ultraviolet-visible-near-infrared spectrometer (UV-Vis-NIR) in the wavelength range of 310-750 nm. The corrosion performance of the coated panels was evaluated by ASTM B117 neutral salt fog testing and cyclic potentiodynamic polarization scans. The latter technique was carried out using a flat cell of 1.0 cm^2 of exposed area (model K0235, Princeton Applied Research) with a saturated calomel electrode (SCE) and platinum mesh counter electrode. A 0.6 wt.% sodium chloride + 0.6 wt.% ammonium sulfate solution in DI water was used as electrolyte. Open circuit potential (OCP) was monitored for 1500 seconds and the cyclic potentiodynamic polarization scans were conducted at 1 mV/s from -0.3 to +0.8 V and then decreased back to -0.25 V respect to OCP.

Results and Discussion

Optical images of cerium-based conversion coatings on AZ31B and AZ91D Mg alloy panels partially exposed to ambient conditions before and after 168 hours of salt spray testing are shown in Figure 1. A color change from pale yellow to almost translucent was observed in the sunlight exposed area of the CeCCs of both alloys compared with the Al foil protected area. Traditionally yellow to orange coatings are obtained when panels are coated through the method described in the experimental procedure. Since the optical properties can be explained by physical and/or chemical changes, the corrosion behavior of both exposed and unexposed areas was studied. The bottom part of Figure 1 shows the panels after salt spray testing. Although the color is different in both areas the corrosion performance is almost identical in each magnesium alloy. No differences in size or number of pits were observed in the different regions for each panel.

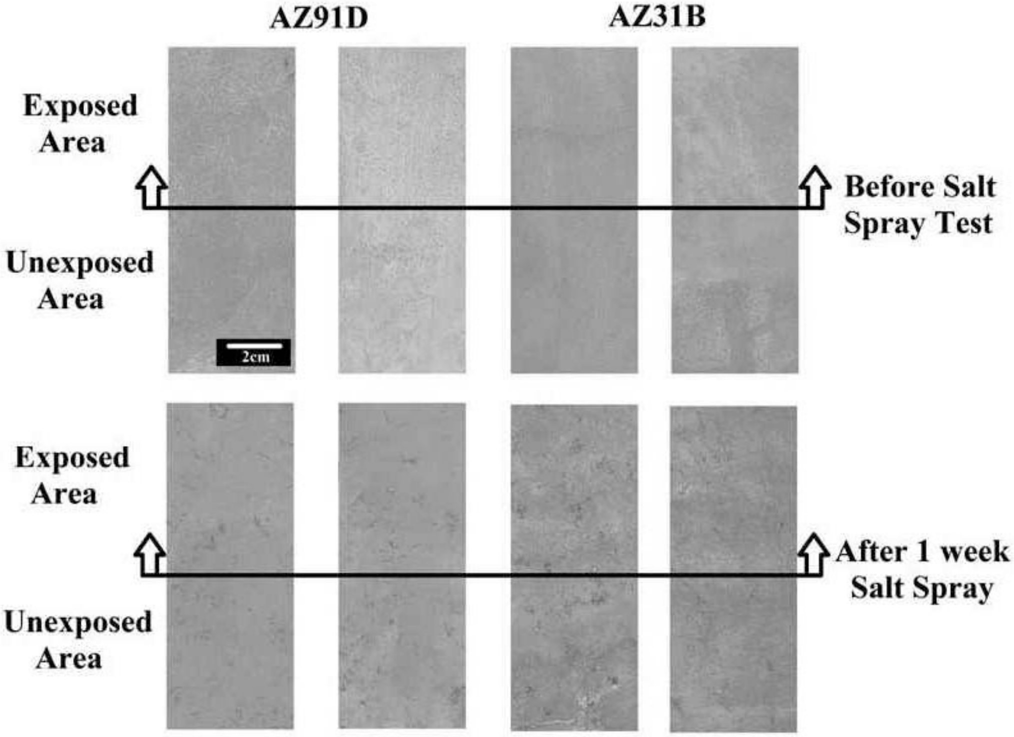


Figure 1. Optical images of cerium-based conversion coatings on AZ91D and AZ31B Mg alloys partially exposed to sunlight before and after 1 week of salt spray testing.

The surface morphologies of the cerium-based conversion coatings on AZ31B and AZ91D Mg alloys after 24 hours of ambient exposure are shown in Figure 2.

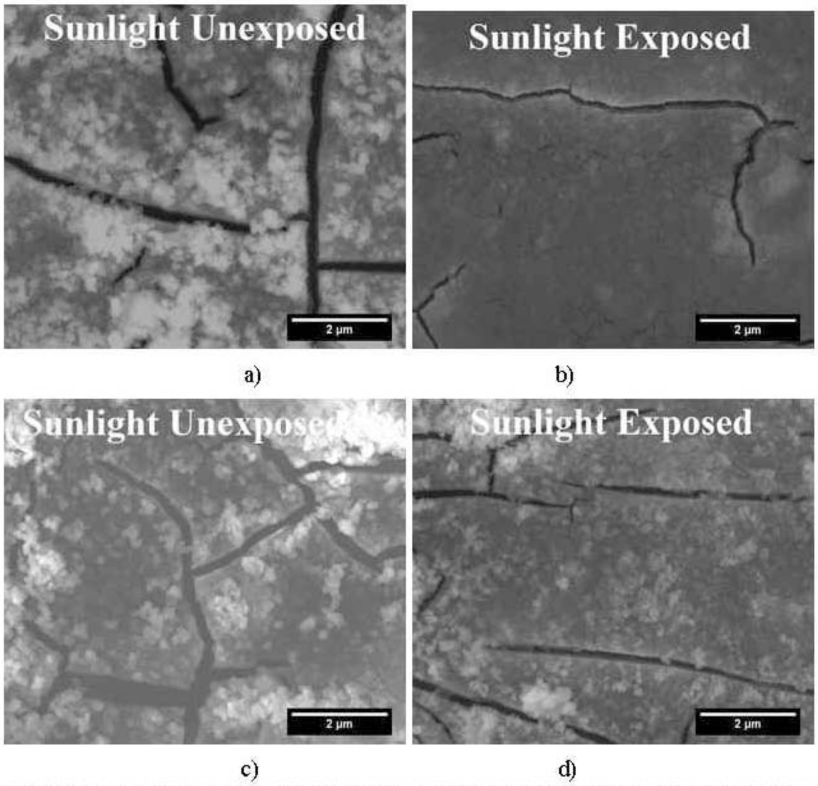
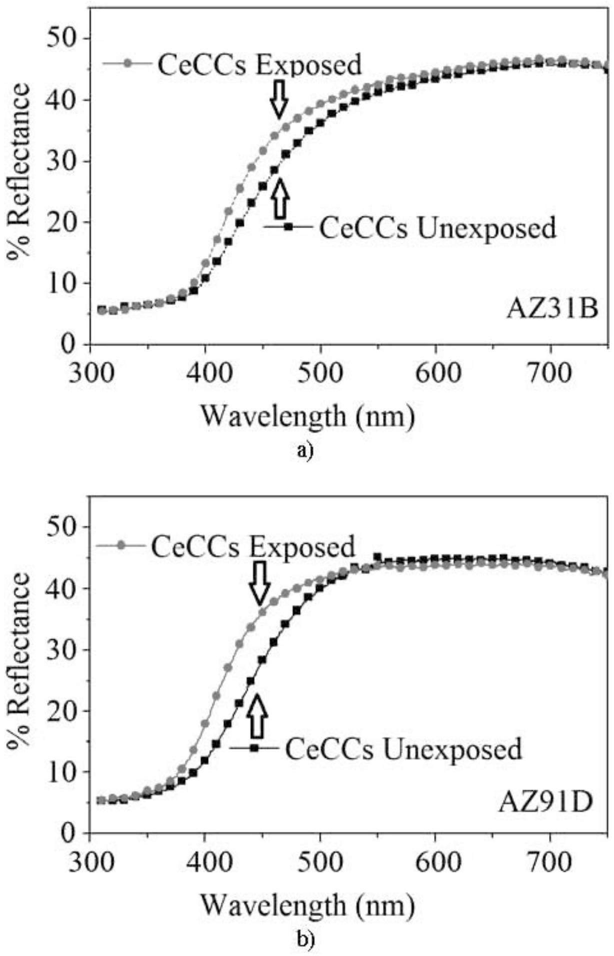


Figure 2. SEM images showing the surface morphologies of CeCCs in the unexposed and exposed sunlight regions on: a), b) AZ31B and c), d) for AZ91D.

Figures 2 a) and 2 c) illustrate the surface morphologies of the CeCC - AZ31B and the CeCC – AZ91D systems without sunlight exposure, respectively. The same uniform cracked surface morphology with small nodular agglomerates has been observed on both magnesium alloys. In addition, this morphology is very similar to the as-coated CeCCs reported previously on magnesium alloys [9-12]. Figures 2 b) and 2 c) reveal the surface structures of the CeCCs on AZ31B and AZ91D after being exposed to 24 hours of sunlight. These coatings showed a slight decrease in cracking and nodule size compared to the unexposed regions of coatings.

The optical reflectance spectra of CeCCs applied on AZ31B and AZ91D Mg alloys with and without being subjected to sunlight are shown in Figures 3 a) and b), respectively. The spectra of the CeCCs subjected to sunlight revealed an increase in the reflectivity at wavelengths between 400 and 500 nm. With this increase, the reflectance of the sunlight exposed samples is consistently higher across the visible range (400-700 nm), appearing lighter than the unexposed regions. Additionally, the spectra of exposed coatings are approximately with the same reflectance value in the visible range which makes the coatings appear white in color. In contrast, the unexposed region presents less reflectance values at wavelengths of 400-500 nm than the rest of the visible range, resulting in a yellowish color.

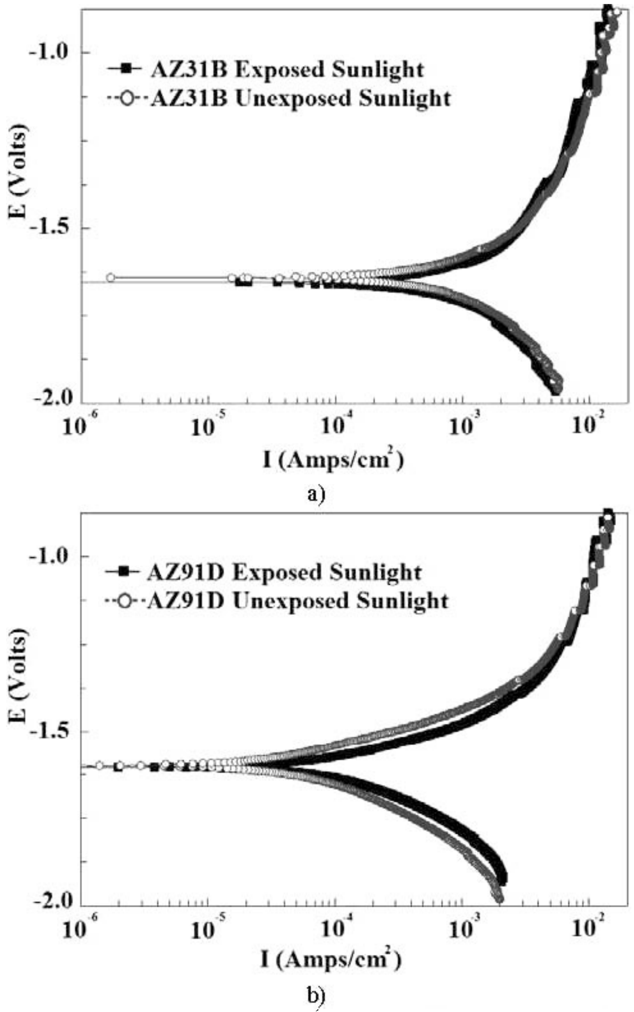


a)

b)

Figure 3. UV-Vis spectra of CeCCs after ambient exposure with and without sunlight exposure on: a) AZ31B and b) AZ91D.

Cyclic potentiodynamic scans of the CeCCs deposited onto AZ31B and AZ91D substrates were measured for ambient exposed regions with and without blocking the sunlight (Figure 4). The corrosion parameters calculated from cyclic potentiodynamic polarization curves are presented in Table I.



a)

b)

Figure 4. Cyclic potentiodynamic polarization comparison of cerium coated unexposed and exposed to sunlight samples on: a) AZ31B Mg alloy and b) AZ91D Mg alloy.

TABLE I. Corrosion parameters derived from the potentiodynamic polarization experiments.

Sample	i_{corr} µA/cm^2	E_{corr} mV$_{SCE}$
AZ31B Unexposed Sunlight	450	-1640
AZ31B Exposed Sunlight	470	-1660
AZ91D Unexposed Sunlight	41	-1600
AZ91D Exposed Sunlight	82	-1600

The Figure 4 a) suggests that corrosion performance of CeCCs with and without sunlight exposure is equivalent since both curves follow the same trend. The calculated corrosion potentials (E_{corr}) and corrosion current densities (i_{corr}) for both regions in AZ31B are basically the same value. The CeCCs on AZ91D exposed and unexposed to sunlight also showed similar corrosion performance. Nevertheless the unexposed region has slightly better corrosion resistance, Figure 4 b). This observation is based on the smaller corrosion current corresponding to the unexposed sample. Although from electrochemical measurements a slight difference between the corrosion performance of exposed and unexposed CeCCs on AZ91D regions is expected, no appreciable variations were found in the salt spray test.

From electrochemical results practically no difference in corrosion behavior was observed for exposed and unexposed regions to sunlight. This observation is consistent with one week in salt spray testing, where panels performed similar in both regions. The optical difference in regions of CeCCs on both Mg alloys after being subjected to direct sunlight has the same tendency; the UV-Vis results showed an increase in the reflectance values at wavelengths in the range of 400 – 500 nm. These results are in agreement with the visual observations and the change in color might be related with the amount of cerium species in each oxidation state. Yellow precipitates have been correlated with high amounts of Ce(IV) species; colorless or translucent precipitates have been identified with larger amounts of Ce(III) species [13]. The morphologies of samples have been studied; fewer cracks and smaller nodule sizes were observed on sunlight exposed panels against unexposed regions.

Conclusions

The exposure of CeCCs on AZ31B and AZ91D Mg alloys to ambient sunlight changed the appearance of the surface. The exposed regions presented different morphologies and reflectance curves but relatively equivalent corrosion properties. The different morphologies observed in ambient sunlight exposed panels do not give clues on why the color could change. Although the surfaces are slightly different after sunlight exposure on both Mg alloys the similar mud-cracking morphology does not suggest different protection performance. The differences found in the reflectance curves are the confirmation of the color change from pale yellow to almost uncolored after 24 hours of sunlight exposure. The decrease of Ce(IV) species on exposed CeCCs might be an explanation for color change, because Ce(IV) species has been related with the yellowish appearance of CeCCs. The studies of CeCCs before and after ambient exposure by ASTM B117 neutral spray testing and electrochemical polarization measurements showed similar results concluding that the sunlight exposed panels did not modify the corrosion properties.

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